

**EXAM 4**

November 22, 2017

*IMPORTANT: Write neatly and lay out solutions clearly. Make sure that you give reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation.  
Give units for all quantities!*

**YOUR NAME** SOLUTIONS

Some data:  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$   $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$   $1 \text{ atm} = 101325 \text{ Pa}$

$$dU = dq + dw \quad dS = dq_{\text{rev}}/T \quad \gamma = C_p/C_v \quad C_p - C_v = nR$$

$$dw = -p_{\text{ex}} dV \quad \text{Heat engine } \varepsilon = (T_h - T_c)/T_h \quad \text{adiabat: } pV^\gamma = \text{const}$$

$$H = U + pV \quad G = H - TS \quad A = U - TS$$

$$k = A \exp(-E_a/(RT)) \quad \text{mean K.E.} = 1.5 k_B T$$

$$d \ln K/d(1/T) = -\Delta H/R \quad \Delta_r G = \Delta G^\circ + RT \ln Q$$

(1) 30 points

Consider the reaction  $A \rightarrow B$  which has the rate law  $v = k[A]^3$ . Initially  $[A] = a_0$ . Prove that  $[A]^{-2} = 2kt + 1/a_0^2$  and use this result to determine the half-life of A. Show work.

Give an example of appropriate units for k.

$$v = k[A]^3 = -\frac{d[A]}{dt} \quad \therefore \quad \frac{d[A]}{[A]^3} = -k dt$$

$$\therefore \int \frac{d[A]}{[A]^3} = \int -k dt \quad \therefore \quad \frac{1}{2} [A]^{-2} = -kt + \text{const}$$

$$\therefore [A]^{-2} = 2kt + \text{const}$$

When  $t=0$ ,  $[A]=a_0 \quad \therefore \text{const} = a_0^{-2}$

$$\therefore [A]^{-2} = 2kt + 1/a_0^2$$

When  $t = t_{1/2}$ ,  $[A] = a_0/2$

$$\therefore \left(\frac{a_0}{2}\right)^{-2} = 2kt_{1/2} + \frac{1}{a_0^2} \quad \therefore \quad 2kt_{1/2} = \frac{4}{a_0^2} - \frac{1}{a_0^2} = \frac{3}{a_0^2}$$

$$\therefore t_{1/2} = \frac{1}{2k} \cdot \frac{3}{a_0^2}$$

$v$  is in conc/time, so  $k$  is in  $\text{conc}^{-2}/\text{time}$ .

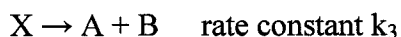
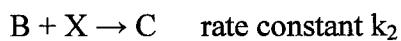
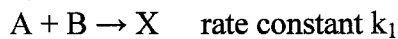
You could use any concentration and time units.

One example is  $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$ .

see exercises A5, B1, B4 and class examples

(2) 30 points

Consider the following mechanism proposed for the overall reaction  $A + 2B \rightarrow C$ :



- i) Assuming that the intermediate X is in a steady state, derive the rate law for formation of C.
- ii) What are the limiting values of the total reaction order as [B] tends to zero and as [B] tends to infinity?

Show work and justify your answers.

$$\begin{aligned} \text{i) } 0 &= \frac{d[X]}{dt} = k_1[A][B] - k_2[B][X] - k_3[X] \\ &\therefore k_1[A][B] = [X](k_2[B] + k_3) \\ &\therefore [X] = \frac{k_1[A][B]}{k_2[B] + k_3} \end{aligned}$$

$$\frac{d[C]}{dt} = k_2[B][X] = \frac{k_1 k_2 [A][B]^2}{k_2[B] + k_3}$$

$$\text{ii) } \lim_{[B] \rightarrow 0} \frac{d[C]}{dt} = \frac{k_1 k_2 [A][B]^2}{k_3}$$

second order in B  
first order in A  

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third order overall

$$\lim_{[B] \rightarrow \infty} \frac{d[C]}{dt} = \frac{k_1 k_2 [A][B]^2}{k_2 [B]}$$

first order in A and B,  
so second order overall.

see exercises E1 and class examples

(3) 20 points

A reaction has  $k = 30 \text{ s}^{-1}$  at 298 K and an activation energy of  $50 \text{ kJ mol}^{-1}$ . Predict the value of  $k$  at 500 K.

$$k = A e^{-\frac{E_a}{RT}} \quad (\text{Arrhenius equation})$$

$$= A e^{-\frac{50000 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}}$$

$$= A e^{-20.18}$$

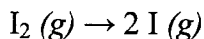
$$\therefore A = e^{+20.18} \cdot k = e^{20.18} \times 30 \text{ s}^{-1} = 1.74 \times 10^{10} \text{ s}^{-1}$$

$$\begin{aligned} \text{At } 500 \text{ K, } k &= 1.74 \times 10^{10} \text{ s}^{-1} \times e^{-\frac{50000 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}}} \\ &= 1.74 \times 10^{10} \text{ s}^{-1} \times e^{-12.03} \\ &= 1.04 \times 10^5 \text{ s}^{-1} \end{aligned}$$

see exercises D1, D2

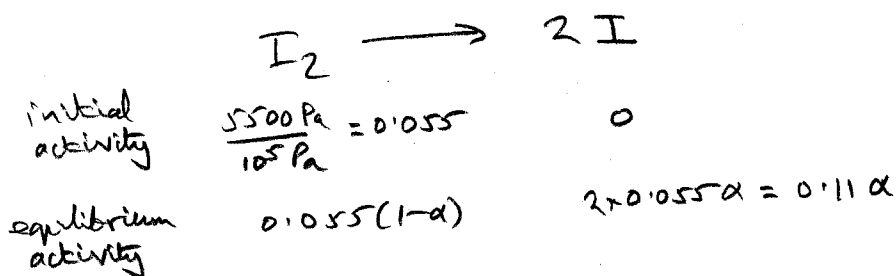
(4) 20 points

At 750 K,  $\Delta_f G^\circ$  of atomic iodine is  $3 \text{ kJ mol}^{-1}$  and the standard state for  $\text{I}_2$  is a gas. Calculate the degree of dissociation  $\alpha$  of  $\text{I}_2$  in a container where 5500 Pa of initially pure  $\text{I}_2$  vapor at 750 K comes to equilibrium:



Comment: do not assume that  $\alpha$  is small compared to 1.

$$\begin{aligned}\Delta G^\circ &= 2\Delta_f G^\circ(\text{I}) - \Delta_f G^\circ(\text{I}_2) = 2 \times 3 \text{ kJ mol}^{-1} - 0 = 6 \text{ kJ mol}^{-1} \\ &= -RT \ln K \quad \therefore K = e^{-\frac{\Delta G^\circ}{RT}} = e^{-\frac{6000 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 750 \text{ K}}} \\ &= e^{-0.962} = 0.382\end{aligned}$$



$$K = \frac{(0.11\alpha)^2}{0.055(1-\alpha)} = \frac{0.22\alpha^2}{1-\alpha}$$

$$\begin{aligned}\therefore K(1-\alpha) &= 0.22\alpha^2 \quad \therefore \alpha^2 = 4.55K - 4.55K\alpha \\ \therefore \alpha^2 - 4.55K + 4.55K\alpha &= 0\end{aligned}$$

now substitute for K:

$$\therefore \alpha^2 - 1.736 + 1.736\alpha = 0$$

$$\therefore \alpha = \frac{-1.736 \pm \sqrt{1.736^2 + 4 \times 1.736}}{2} = \frac{-1.736 \pm 3.156}{2}$$

and  $\alpha$  must be positive so  $\alpha = \frac{-1.736 + 3.156}{2} = 0.710$ ,

see exercises 6A.5, 6B.4, class examples and the last test.